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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Daniel James TWITCHEN, et al.

GAU: 1765

SERIAL NO: 10/655,581

FILED: September 5, 2003

FOR: COLOURED DIAMOND

REQUEST FOR PRIORITY

COMMISSIONER FOR PATENTS
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SIR:

- ☐ Full benefit of the filing date of U.S. Application Serial Number , filed , is claimed pursuant to the provisions of 35 U.S.C. §120.
- ☐ Full benefit of the filing date(s) of U.S. Provisional Application(s) is claimed pursuant to the provisions of 35 U.S.C. §119(e): Application No. Date Filed

- ☒ Applicants claim any right to priority from any earlier filed applications to which they may be entitled pursuant to the provisions of 35 U.S.C. §119, as noted below.

In the matter of the above-identified application for patent, notice is hereby given that the applicants claim as priority:

| <u>COUNTRY</u> | <u>APPLICATION NUMBER</u> | <u>MONTH/DAY/YEAR</u> |
|----------------|---------------------------|-----------------------|
| Great Britain | 0130004.5 | December 14, 2001 |

Certified copies of the corresponding Convention Application(s)

- ☒ are submitted herewith
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- ☐ were submitted to the International Bureau in PCT Application Number
Receipt of the certified copies by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.
- ☐ (A) Application Serial No.(s) were filed in prior application Serial No. filed ; and
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Respectfully Submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.
Norman F. Oblon

Customer Number

22850

Tel. (703) 413-3000
Fax. (703) 413-2220
(OSMMN 05/03)

Frederick D. Vastine
Registration No. 27,013



INVESTOR IN PEOPLE

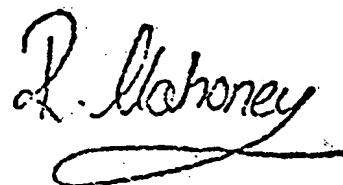

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PA132213/P (P029097GB)

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3. Full name, address and postcode of the or of
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**Diamanx Products Limited
Isle of Man Freeport
Ballasalla
IM99 6AQ
Isle of Man**

04153752002

Patents ADP number (if you know it)

If the applicant is a corporate body, give the
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Isle of Man, U.K.

4. Title of the invention

Coloured Diamond

5. Name of your agent (if you have one)

Carpmaels & Ransford

"Address for service" in the United Kingdom
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**43 Bloomsbury Square
London
WC1A 2RA**

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83001

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Description

23 ✓

Claim(s)

Abstract

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Date

Carpmaels & Ransford 14th December 2001
Carpmaels & Ransford

12. Name and daytime telephone number of person to contact in the United Kingdom
- Mr. A.J. Jones / Ms. Janet Scopes 020-7242 8692

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COLOURED DIAMOND

BACKGROUND OF THE INVENTION

This invention relates to a method of producing by chemical vapour deposition (hereinafter referred to as CVD) coloured single crystal diamond, and in one aspect a method of producing fancy coloured diamond, these coloured diamonds being suitable, for example, for preparation for ornamental purposes.

Intrinsic diamond has an indirect band gap of 5.5 eV and is transparent in the visible part of the spectrum. Introducing defects or colour centres, as they will be called, which have associated energy levels within the band gap gives the diamond a characteristic colour which is dependent on the type and concentration of the colour centres. This colour can result from either absorption or photoluminescence or some combination of these two. One example of a common colour centre present in synthetic diamond is nitrogen which, when sitting on a substitutional lattice site in the neutral charge state, has an associated energy level ~ 1.7 eV below the conduction band - the resulting absorption gives the diamond a characteristic yellow/brown colour.

Methods of depositing material such as diamond on a substrate by CVD are now well established and have been described extensively in the patent and other literature. Where diamond is being deposited on a substrate, the method generally involves providing a gas mixture which, on dissociation, can provide hydrogen or a halogen (e.g. F, Cl) in atomic form and C or carbon-containing radicals and other reactive species, e.g. CH_x , CF_x wherein x can be 1 to 4. In

addition, oxygen containing sources may be present, as may sources for nitrogen, and for boron. Nitrogen can be introduced in the synthesis plasma in many forms; typically these are N_2 , NH_3 , air and N_2H_4 . In many processes inert gases such as helium, neon or argon are also present. Thus, a typical source gas mixture will contain hydrocarbons C_xH_y wherein x and y can each be 1 to 10 or halocarbons $C_xH_yHal_z$ wherein x and z can each be 1 to 10 and y can be 0 to 10 and optionally one or more of the following: CO_x , wherein x can be 0.5 to 2, O_2 , H_2 , N_2 , NH_3 , B_2H_6 and an inert gas. Each gas may be present in its natural isotopic ratio, or the relative isotopic ratios may be artificially controlled; for example hydrogen may be present as deuterium or tritium, and carbon may be present as ^{12}C or ^{13}C . Dissociation of the source gas mixture is brought about by an energy source such as microwaves, RF (radio frequency) energy, a flame, a hot filament or jet based technique and the reactive gas species so produced are allowed to deposit onto a substrate and form diamond.

CVD diamond may be produced on a variety of substrates. Depending on the nature of the substrate and details of the process chemistry, polycrystalline or single crystal CVD diamond may be produced.

It is well known that post growth treatment such as irradiation with sufficiently energetic particles (electron, neutron, gamma etc) to produce lattice defects (interstitials and vacancies) and suitable annealing can result in the formation of colour centres, such as the nitrogen vacancy [N-V] colour centre, which can give the diamond a desirable colour (see for example EP 0 615 954 A1, EP 0 326 856 A1 and references therein). Further characteristics and artificial production of colour centres is discussed in detail by John Walker in the Reports on Progress in Physics, Vol. 42 1979. The artificial production method of colour centres outline therein comprises the steps of forming lattice defects in crystals by electron beam irradiation and, if necessary performing annealing to cause said lattice defects to combine with nitrogen atoms contained in the crystals. However, there are limitations to the colours and uniformity that can be produced

as a consequence of competitive defect formation and because of the strong sector dependence associated with defects such as nitrogen in diamond.

The colour of a diamond coloured by utilising this post growth colour centre formation method is the colour of the rough diamond combined with the colour of the colour centre produced. In order to obtain the ornamental value desired, and thus achieve a combination of high transparency and fancy colour, it has been usual practice to use diamonds that were initially either transparent or light yellow. In this invention there is no post growth treatment as the colour centres are introduced by a careful selection of growth conditions. There are many reports in the literature of homoepitaxial CVD growth on high pressure high temperature (HPHT) synthetic and natural diamond substrates. Although there are only a few reports of thick layers ($>100\text{ }\mu\text{m}$), these tend to have an unattractive brown colour which results mainly from absorption related to low crystalline quality defects and graphitic/metallic inclusions and which are reported to increase with growth thickness. Even if growth conditions were chosen to allow incorporation of colour centres that would give the diamond a desirable colour, this desirable colour would be masked by the dominant absorption relating to the low quality nature of the diamond crystal structure.

SUMMARY OF THE INVENTION

According to a first aspect of the invention, there is provided a coloured single crystal diamond layer, preferably a fancy coloured single crystal diamond layer, and more preferably a fancy brown coloured single crystal diamond layer, synthesised by CVD, prepared or suitable for preparation as a cut stone for ornamental application. The CVD diamond layer has a thickness $>1\text{ mm}$, and preferably $>2\text{ mm}$ and more preferably $>3\text{ mm}$. One or more of the following characteristics (i), (ii) and (iii) are observable in the majority volume of the layer, where the majority volume comprises at least 55%, and preferably at

least 80%, and more preferably at least 95% of the whole volume of the layer. Preferably the majority volume of the layer is formed from a single growth sector.

- (i) The majority volume of the CVD diamond layer contains one or more of the defect and impurity related colour centres that contribute to the absorption spectrum of the diamond as detailed in the absorption coefficient column of the table below:

| Designation | Starts | Ends | Peak | Absorption coefficient (at peak) |
|--------------|---|---------|------------------------|--|
| 270 nm | 220 nm | 325 nm | 270 nm | 0.1 cm ⁻¹ – 30 cm ⁻¹ preferably 0.4 cm ⁻¹ – 10 cm ⁻¹ more preferably 0.8 cm ⁻¹ – 6 cm ⁻¹ |
| 350 nm/broad | 270 nm | 450 nm | 350 nm +/- 10 nm | 0.3 cm ⁻¹ – 20 cm ⁻¹ preferably 1.0 cm ⁻¹ – 8 cm ⁻¹ more preferably 1.5 cm ⁻¹ – 6 cm ⁻¹ |
| 510 nm/broad | 420 nm | 640 nm | 510 nm +/- 50 nm | 0.1 cm ⁻¹ – 10 cm ⁻¹ preferably 0.2 cm ⁻¹ – 4 cm ⁻¹ more preferably 0.4 cm ⁻¹ – 2 cm ⁻¹ |
| 570/637 nm | 500 nm | 640 nm | 570 nm | 0.1 cm ⁻¹ – 5 cm ⁻¹ preferably 0.3 cm ⁻¹ – 3 cm ⁻¹ more preferably 0.3 cm ⁻¹ – 1.5 cm ⁻¹ |
| 1357 nm | 550 nm | 1360 nm | 1357 nm | 0.1 cm ⁻¹ – 5 cm ⁻¹ preferably 1 cm ⁻¹ – 5 cm ⁻¹ more preferably 2 cm ⁻¹ – 5 cm ⁻¹ |
| | Rising background of form Absorption coefficient (cm ⁻¹) = $C \times \lambda^{-3}$ (C=constant, λ in μ m) | | | Contribution at 510 nm is: < 3 cm ⁻¹ preferably < 1.5 cm ⁻¹ more preferably < 0.8 cm ⁻¹ |

- (ii) The majority volume of the CVD diamond layer contains defect and impurity related centres that contribute to the luminescence spectrum as detailed in the Normalised luminescence intensity column of the table below, when measured in the prescribed manner using Ar ion 514nm laser excitation at 77K:

| Designation | Starts | Ends | Peak | Normalised luminescence intensity of zero phonon line at 77K |
|-------------|--------|--------|--------|---|
| 575 nm | 570 nm | 680 nm | 575 nm | 0.02 - 80 preferably 0.05 - 60 more preferably 0.2 - 40 |
| 637 nm | 635 | 800 | 637 nm | 0.01 - 300 preferably 0.02 - 200 more preferably 0.03 - 100 |

- (iii) The majority volume of the CVD diamond layer exhibits a ratio of normalised 637 nm/575 nm luminescence, measured in the manner described herein, which is in the range 0.2 - 10, and preferably in the range 0.5 - 8, and more preferably in the range 2 - 5.

The present invention provides a coloured single crystal diamond which may induce a transparent and brilliant sensation in the mind and is desirable. A particular aspect of the invention is the provision of fancy coloured gemstones, the term fancy referring to a gem trade classification of stronger and more desirable colours in diamond. Even more particularly the invention can provide a range of fancy brown colours, and example being fancy light pink brown. This invention further provides for a thick (>1 mm) diamond layer with uniform properties through its thickness so that any desirable colour is not quenched or hidden by defects related to low crystalline quality. The fanciness of the colours was originally not anticipated, nor the degree to which they could be controlled by choosing appropriate synthesis and substrate conditions. No post growth treatment is needed to produce these colours. In fact many of these colours are impossible to produce using post growth treatments, as a consequence of the relative colour centre formation mechanisms that compete during irradiation and annealing. In addition, characteristics associated with the CVD growth mechanism that can result in absorption at ~350, ~510 and ~1360 nm are important for the final colour produced, but these centres are not present in natural or other synthetic diamond. Consequently the colours

achieved are unique to CVD diamond, and more particularly to CVD diamond made by the method of the invention.

In addition, the majority volume of the layer may exhibit one or more of the following properties:

1. High crystalline quality as determined by a low density of extended defects, related factors such as narrow Raman line width, relatively featureless X-ray topography and narrow rocking curve, mechanical integrity, strength and mechanical processability of the material to form highly polished surfaces and edges. In this context high quality excludes quality factors normally requiring the absence of N, including features such as: the N impurities themselves and also associated point defects including H related defects and vacancies, electronic based properties such as mobility and charge collection distance which are very sensitive to scattering centres and traps, and the specific optical absorption and luminescence characteristics induced by the presence of the added nitrogen and the associated defects.
2. A crystal morphology characteristic of nitrogen being added into the gas phase such that a up to 100% usable area increase over the original substrate area can be obtained.
3. A level of any single impurity: Fe, Si, P, S, Ni, Co, Al, Mn of not greater than 1 ppm and a total impurity content of not greater than 5 ppm. In the above, "impurity" excludes hydrogen and its isotopic forms.
4. In EPR, a spin density $<1 \times 10^{17} \text{ cm}^{-3}$ and more typically $<5 \times 10^{16} \text{ cm}^{-3}$ at $g=2.0028$. In single crystal diamond this line at

$g = 2.0028$ is related to lattice defect concentrations and is typically large in natural type IIa diamond, in CVD diamond plastically deformed through indentation, and in poor quality homoepitaxial diamond.

5. X-ray topography showing features related to growth where $\langle 100 \rangle$ edges of the original substrate are grown out to form $\langle 110 \rangle$ edges.

The novel fancy coloured single crystal CVD diamond of the invention may be made by a method that forms yet another aspect of the invention. This method includes the steps of providing a diamond substrate having a surface which is substantially free of crystal defects, providing a source gas, dissociating the source gas and allowing homoepitaxial diamond growth on the surface which is substantially free of crystal defects.

In the method of this invention, additions of nitrogen to the synthesis plasma, in addition to producing colour centres in the diamond, can be used beneficially to cause morphological changes to the growing single crystal CVD diamond. Specifically, the addition of nitrogen to the gas phase can be used to enhance the size of the $\{100\}$ growth sector and reduce the size of competing growth sectors such as the $\{111\}$. This means that, for growth on a $\{100\}$ plate, the addition of nitrogen enables the growth to remain substantially $\{100\}$ growth sector. In addition, where the initial substrate sides are $\{100\}$, with $\langle 100 \rangle$ edges bounding the top $\{100\}$ face, these sides can be made to demonstrate lateral growth until the edges bounding the vertical $\{100\}$ growth are predominantly $\langle 110 \rangle$, increasing the area of the $\{100\}$ face forming the $\{100\}$ growth sector by a factor of two over the area of the original substrate.

DETAILED DESCRIPTION OF THE INVENTION

Absorption spectroscopy of homoepitaxial CVD diamond

The UV/visible absorption spectrum of type Ib diamond contains features associated with single substitutional nitrogen. These include an absorption coefficient maximum at 270 nm and, to longer wavelengths, a gradual decrease in absorption coefficient between approximately 300 nm and 500 nm, with signs of a broad absorption band at approximately 365 nm. Although the effect of single substitutional nitrogen on the absorption spectrum is greatest in the ultra-violet, it is the weaker absorption that extends into the visible region of the spectrum that affects the colour of the type Ib diamond and gives it the characteristic yellow/brown colour of type Ib diamond. This particular colour when strong and displaying the brown element is generally judged to be undesirable in a gemstone.

The UV/visible absorption spectrum of homoepitaxial CVD diamond doped with nitrogen typically contains a contribution from single substitutional nitrogen with the spectral characteristics described above. In addition to single substitutional nitrogen, nitrogen doped homoepitaxial CVD diamond typically contains some nitrogen in the form of nitrogen vacancy centres. When the N-V centre is electrically neutral $[N-V]^0$ it gives rise to absorption with a zero phonon line at 575 nm. When the N-V centre is negatively charged $[N-V]^-$ it gives rise to absorption with a zero-phonon line at 637 nm and an associated system of phonon bands with an absorption maximum at approximately 570 nm. At room temperature, the normal temperature for observation of gemstones, the absorption bands of these two charge states of the N-V centre merge into a broad band from about 500 nm - 640 nm. This absorption band is in the yellow part of the visible spectrum, and as a result of this absorption the crystals can

exhibit a complementary pink/purple colour. This absorption plays an important part in determining the colour of the diamond of this invention.

The absorption spectrum of nitrogen doped homoepitaxial CVD diamond may also contain a line at 1357 nm in the near-infrared. This has been associated with a hydrogen-related colour centre and for samples for which this is very strong, associated phonon bands can give rise to significant absorption at the red end of the visible spectrum. In combination with absorption at the blue end of the spectrum (relating to the presence of single substitutional nitrogen), this absorption can give the diamond a green colour.

The UV/visible absorption spectra of low quality homoepitaxial CVD diamond, show a gradual rise in measured absorption from the red to the blue region of the spectrum and into the ultra-violet. There may also be contributions from scattering. The spectra generally contain no other features, apart from those related to single substitutional nitrogen. This absorption spectrum gives an undesirable brown colour and such diamond often contains clearly visible graphitic inclusions. Such diamond is unsuitable as a gemstone material for these reasons and because it cannot in general be grown to substantial thicknesses without severe degradation of the crystal quality.

The coloured single crystal CVD diamond of the invention is of high crystalline quality and is substantially free of crystal defects other than the intentionally added nitrogen and also the vacancies that are a product in any diamond synthesis process and a beneficial aspect of this process. Vacancies are simply the absence of carbon atoms on lattice sites. CVD diamond synthesis is unique in that it occurs at a temperature just above that at which vacancies are mobile. Vacancies are thus very effectively used in the formation of colour centres during growth. As a consequence of their mobility and tendency to form [N-V] defects less than 1 ppm and more preferably less than 0.1 ppm isolated vacancies remain at the end of the growth period. This is important to the fancy

colours produced since isolated vacancies have their own absorption that gives the diamond a dark green/black colour.

The absorption spectrum of the nitrogen-doped diamond of the current invention contains additional contributions that are not present in natural, HPHT synthetic diamond or low quality CVD diamond. These include two broad bands centred at approximately 350 nm and 510 nm. These bands are thought to be associated with very localised disruption of the diamond bonding that does not generally lead to degradation of crystal quality.

The band at approximately 350 nm is distinct from the broad feature in that region of the spectrum of ordinary type Ib spectrum and distorts the spectrum of ordinary type Ib diamond to an extent dependent on the concentration of the centre responsible relative to the single substitutional nitrogen.

Similarly the band centred at approximately 510 nm can overlap absorption relating to negative nitrogen-vacancy centres and the visible absorption relating to single substitutional nitrogen.

The overlapping of the various contributions to the absorption spectra can cause the bands at approximately 350 and 510 nm to give rise to broad shoulders in the absorption spectrum rather than distinct maxima. These contributions to absorption do however have a very significant effect on the relative absorption coefficients of the diamond at wavelengths in the spectral region between 400 and 600 nm where the eye is very sensitive to small differences. They therefore make an important contribution to the perceived colour of the diamond. Together with the luminescence characteristics noted below, these absorption characteristics can give diamond gemstones produced from such diamond desirable fancy brown colours, including fancy dark brown, orange brown and pink brown.

The width and position in the spectrum of these bands can vary, presumably because of differences in the local disruption of diamond bonding. The position of peak maxima is most easily ascertained by using the second differential of the spectrum. It has been found that absorption spectra can generally be deconstructed into the following approximate components.

- 1) Single substitutional nitrogen component with an absorption coefficient at 270 nm that is generally within the range 0.4 cm^{-1} and 10 cm^{-1} and an absorption coefficient at 425 nm that generally lies between 0.04 cm^{-1} and 1 cm^{-1} .
- 2) An absorption band centred at 3.54 eV (350 nm) $\pm 0.2 \text{ eV}$ with a FWHM of approximately 1 eV and a maximum contribution to the absorption spectrum generally between 1 and 8 cm^{-1} at its centre.
- 3) An absorption band centred at 2.43 eV (510 nm) $\pm 0.4 \text{ eV}$ with a FWHM of approximately 1 eV and a maximum contribution to the absorption spectrum generally between 0.2 and 4 cm^{-1} at its centre.
- 4) A small residual wavelength dependent component of the measured absorption coefficient (in cm^{-1}) that is found to have a wavelength dependence of the following approximate form: $c \times (\text{wavelength in microns})^{-3}$ where $c < 0.2$ such that the contribution of this component at 510 nm is generally less than 1.5 cm^{-1} .

Luminescence

The colour of a diamond is principally dependent on its absorption spectrum but it can also be influenced by its luminescence properties. This may be particularly the case for certain viewing conditions. For example, the luminescence will have the greatest effect when the diamond is viewed from a

small distance under illumination with light that contains a strong component in a wavelength range that excites the luminescence most efficiently.

The diamond of the present invention shows strong luminescence from nitrogen-vacancy colour centres. The neutral and negatively charged N-V centres have their zero-phonon lines at 575 nm and 637 nm, respectively, and have absorption band systems on the shorter wavelength side of these zero-phonon lines. Light of wavelengths within the range covered by these absorption bands can be absorbed by these colour centres and give rise to luminescence with a spectrum which is characteristic of these centres. The luminescence from the neutral N-V centre is predominantly orange. That from the negatively charged N-V centre is red.

The negatively charged N-V centre is a relatively strong absorber, giving rise to an absorption band system with a maximum at around 570 nm. Some of the energy absorbed at these centres is re-emitted as luminescence. In contrast, the neutral N-V centre has a very small effect on the absorption spectrum and the energy absorbed is typically converted to luminescence with a high efficiency.

N-V centres in the vicinity of an electron donor, such as single substitutional nitrogen, are negatively charged, while isolated N-V centres are neutral. The effect of a given concentration of N-V centres on the colour of a diamond therefore depends on the concentration and relative distribution of electron donors. For example, N-V centres in diamond containing a high concentration of N will contribute to the colour predominantly via absorption of light by negatively charged N-V centres with a smaller contribution coming from luminescence. In the case of diamond containing low concentrations of electron donors such as nitrogen, luminescence from neutral N-V centres can make a more important contribution.

Luminescence measurement and quantification

As a result of variations in the importance of non-radiative paths, luminescence properties of diamond samples cannot in general be deduced directly from the concentrations of the various contributing centres as determined by absorption spectroscopy. Quantitative luminescence properties of diamond samples can, however be specified by normalising the integrated intensities of relevant luminescence lines or bands relative to the integrated intensity of diamond Raman scattering collected under the same conditions.

The table below lists the results of quantitative luminescence measurements made on a range of single crystal CVD diamond samples of the invention. In each case, the measurements were made after removal of the {100} substrate on which each was grown. The growth conditions favoured the formation of predominantly <100> sector diamond samples with uniform luminescence properties as judged by luminescence imaging. Any small additional sectors with different luminescence properties were removed before the measurements were made.

The luminescence was excited at 77K with a 300 mW 514 nm argon ion laser beam and spectra were recorded using a Spex 1404 spectrometer equipped with a holographic grating (1800 grooves/mm) and a Hamamatsu R928 photomultiplier. The data were corrected to allow for spectral response function of the spectrometer system, derived using a standard lamp with a known spectral output.

| | Normalised | Normalised | I(637)/I(575) |
|--------|------------|------------|---------------|
| Sample | I(575) | I(637) | |
| 404 | 1.929 | 6.880 | 3.566 |
| 407 | 5.808 | 17.65 | 3.039 |
| 409 | 3.116 | 10.07 | 3.233 |
| 410 | 1.293 | 4.267 | 3.299 |
| 412 | 2.703 | 7.367 | 2.725 |
| 414 | 17.09 | 52.29 | 3.058 |
| 415 | 19.06 | 41.92 | 2.198 |
| 416 | 17.02 | 70.00 | 4.111 |
| 417 | 32.86 | 69.77 | 2.123 |
| 418 | 29.34 | 61.31 | 2.089 |
| 423 | 6.985 | 7.019 | 1.004 |
| 424 | 51.41 | 101.8 | 1.981 |
| 425 | 68.22 | 277.4 | 4.067 |
| 426 | 16.17 | 29.23 | 1.807 |
| 434 | 4.929 | 4.378 | 0.8883 |
| 435 | 0.4982 | 1.223 | 2.455 |
| 437 | 0.3816 | 0.2224 | 0.5828 |
| 439 | 4.24 | 2.891 | 0.6818 |
| 505 | 0.00954 | 0.04031 | 4.225 |
| 507c | 0.3455 | 2.347 | 6.793 |
| 507b | 0.106 | 0.03252 | 0.3068 |
| 511b | 4.611 | 4.211 | 0.9134 |
| 501 | 2.586 | 1.959 | 0.7577 |
| 512 | 7.282 | 7.686 | 1.055 |
| 515 | 0.01886 | 0.01932 | 1.024 |
| 520 | 0.1802 | 0.5421 | 3.008 |
| 521 | 0.0402 | 0.03197 | 0.7936 |
| 513 | 0.0243 | 0.01765 | 0.7240 |
| 509 | 25.22 | 13.87 | 0.5498 |
| 511c | 0.0371 | 0.01112 | 0.2997 |
| 513b | 1.091 | 1.262 | 1.155 |
| 513c | 0.1717 | 0.2224 | 1.295 |
| 513d | 1.992 | 0.7645 | 0.3836 |
| 510b | 0.3922 | 0.6963 | 1.775 |
| 510c | 0.1643 | 0.6268 | 3.815 |
| 510d | 1.091 | 0.6811 | 0.6238 |
| 514a | 126.6 | 56.57 | 0.4466 |
| 514b | 101.3 | 50.79 | 0.5012 |
| 514c | 141.6 | 67.83 | 0.4789 |

It is important for the production of high crystalline quality (herein defined) thick single crystal CVD diamond with properties suitable for coloured gem stones that growth takes place on a diamond surface which is substantially free of crystal defects. In this context, defects primarily mean dislocations and micro cracks, but also include twin boundaries, point defects not intrinsically associated with the dopant N atoms, low angle boundaries and any other extended disruption to the crystal lattice. Preferably the substrate is a low birefringence type Ia natural, Ib or IIa high pressure/high temperature synthetic diamond or a CVD synthesised single crystal diamond.

The quality of growth on a substrate which is not substantially free of defects rapidly degrades as the layer grows thicker and as the defect structures multiply, causing general crystal degradation, twinning and renucleation.

The defect density is most easily characterised by optical evaluation after using a plasma or chemical etch optimised to reveal the defects (referred to as a revealing plasma etch), using for example a brief plasma etch of the type described below. Two types of defects can be revealed:

- 1) Those intrinsic to the substrate material quality. In selected natural diamond the density of these defects can be as low as $50/\text{mm}^2$ with more typical values being $10^2/\text{mm}^2$, whilst in others it can be $10^6/\text{mm}^2$ or greater.
- 2) Those resulting from polishing, including dislocation structures and microcracks forming chatter tracks along polishing lines. The density of these can vary considerably over a sample, with typical values ranging from about $10^2/\text{mm}^2$, up to more than $10^4/\text{mm}^2$ in poorly polished regions or samples.

The preferred low density of defects is such that the density of surface etch features related to defects, as described above, are below $5 \times 10^3/\text{mm}^2$, and more preferably below $10^2/\text{mm}^2$.

The defect level at and below the substrate surface on which the CVD growth takes place may thus be minimised by careful preparation of the substrate. Included here under preparation is any process applied to the material from mine recovery (in the case of natural diamond) or synthesis (in the case of synthetic material) as each stage can influence the defect density within the material at the plane which will ultimately form the substrate surface when preparation as a substrate is complete. Particular processing steps may include conventional diamond processes such as mechanical sawing, lapping and polishing (in this application specifically optimised for low defect levels), and less conventional techniques such as laser processing or ion implantation and lift off techniques, chemical/mechanical polishing, and both liquid and plasma chemical processing techniques. In addition, the surface R_q (root mean square deviation of surface profile from flat measured by stylus profilometer, preferably measured over 0,08 mm length) should be minimised, typical values prior to any plasma etch being no more than a few nanometers, i.e. less than 10 nanometers.

One specific method of minimising the surface damage of the substrate, is to include an *in situ* plasma etch on the surface on which the homoepitaxial diamond growth is to occur. In principle this etch need not be *in situ*, nor immediately prior to the growth process, but the greatest benefit is achieved if it is *in situ*, because it avoids any risk of further physical damage or chemical contamination. An *in situ* etch is also generally most convenient when the growth process is also plasma based. The plasma etch can use similar conditions to the deposition or diamond growing process, but with the absence of any carbon containing source gas and generally at a slightly lower temperature to give better control of the etch rate. For example, it can consist of one or more of:

- (i) an oxygen etch using predominantly hydrogen with optionally a small amount of Ar and a required small amount of O₂. Typical oxygen etch conditions are pressures of 50-450 x 10² Pa, an etchin gas containing an oxygen content of 1 to 4 percent, an argon content of 0 to 30 percent and the balance hydrogen, all percentages being by volume, with a substrate temperature 600-1100°C (more typically 800°C) and a typical duration of 3-60 minutes.
- (ii) a hydrogen etch which is similar to (i) but where the oxygen is absent.
- (iii) alternative methods for the etch not solely based on argon, hydrogen and oxygen may be used, for example, those utilising halogens, other inert gases or nitrogen.

Typically the etch consists of an oxygen etch followed by a hydrogen etch and then moving directly into synthesis by the introduction of the carbon source gas. The etch time/temperature is selected to enable remaining surface damage from processing to be removed, and for any surface contaminants to be removed, but without forming a highly roughened surface and without etching extensively along extended defects such as dislocations which intersect the surface and thus cause deep pits. As the etch is aggressive, it is particularly important for this stage that the chamber design and material selection for its components be such that no material is transferred by the plasma into the gas phase or to the substrate surface. The hydrogen etch following the oxygen etch is less specific to crystal defects rounding off the angularities caused by the oxygen etch which aggressively attacks such defects and providing a smoother, better surface for subsequent growth.

The surface or surfaces of the diamond substrate on which the CVD diamond growth occurs are preferably the {100}, {110}, {113} or {111} surfaces. Due to processing constraints, the actual sample surface orientation can differ from these ideal orientations up to 5°, and in some cases up to 10°, although this is less desirable as it adversely affects reproducibility.

It is also important in the method of the invention that the impurity content of the environment in which the CVD growth takes place is properly controlled. More particularly, the diamond growth must take place in the presence of an atmosphere containing substantially no contaminants other than the intentionally added nitrogen which should be controlled to better than 500 parts per billion (as a molecular fraction of the total gas volume) or 5% in the gas phase, whichever is the larger, and preferably to better than 300 parts per billion (as a molecular fraction of the total gas volume) or 3% in the gas phase, whichever is the larger, and more preferably to better than 100 parts per billion (as a molecular fraction of the total gas volume) or 1% in the gas phase, whichever is the larger. Measurement of absolute and relative nitrogen concentration in the gas phase at concentrations as low as 100 ppb requires sophisticated monitoring equipment such as that which can be achieved, for example, by gas chromatography. An example of such a method is now described:

Standard gas chromatography (GC) art consists of: a gas sample stream is extracted from the point of interest using a narrow bore sample line, optimised for maximum flow velocity and minimum dead volume, and passed through the GC sample coil before being passed to waste. The GC sample coil is a section of tube coiled up with a fixed and known volume (typically 1cm³ for standard atmospheric pressure injection) which can be switched from its location in the sample line into the carrier gas (high purity He) line feeding into the gas chromatography columns. This places a sample of gas of known volume into

the gas flow entering the column; in the art, this procedure is called sample injection.

The injected sample is carried by the carrier gas through the first GC column (filled with a molecular sieve optimised for separation of simple inorganic gases) and is partially separated, but the high concentration of primary gases (e.g. H₂, Ar) causes column saturation which makes complete separation of, for example nitrogen difficult. The relevant section of the effluent from the first column is then switched into the feed of a second column, thereby avoiding the majority of the other gases being passed into the second column, avoiding column saturation and enabling complete separation of the target gas (N₂). This procedure is called "heart-cutting".

The output flow of the second column is put through a discharge ionisation detector (DID), which detects the increase in leakage current through the carrier gas caused by the presence of the sample. Chemical structure is identified by the gas residence time which is calibrated from standard gas mixtures. The response of the DID is linear over more than 5 orders of magnitude, and is calibrated by use of special calibrated gas mixtures, typically in the range of 10-100 ppm, made by gravimetric analysis and then verified by the supplier. Linearity of the DID can be verified by careful dilution experiments.

This known art of gas chromatography has been further modified and developed for this application as follows: The processes being analysed here are typically operating at $50 - 500 \times 10^2$ Pa. Normal GC operation uses the excess pressure over atmospheric pressure of the source gas to drive the gas through the sample line. Here, the sample is driven by attaching a vacuum pump at the waste end of the line and the sample drawn through at below atmospheric pressure. However, whilst the gas is flowing the line impedance can cause significant pressure drop in the line, affecting calibration and

sensitivity. Consequently, between the sample coil and the vacuum pump is placed a valve which is shut for a short duration before sample injection in order to enable the pressure at the sample coil to stabilise and be measured by a pressure gauge. To ensure a sufficient mass of sample gas is injected, the sample coil volume is enlarged to about 5 cm³. Dependent on the design of the sample line, this technique can operate effectively down to pressures of about 70×10^2 Pa. Calibration of the GC is dependent on the mass of sample injected, and the greatest accuracy is obtained by calibrating the GC using the same sample pressure as that available from the source under analysis. Very high standards of vacuum and gas handling practice must be observed to ensure that the measurements are correct.

The point of sampling may be upstream of the synthesis chamber to characterise the incoming gases, within the chamber to characterise the chamber environment, or downstream of the chamber.

The source gas may be any known in the art and will contain a carbon-containing material which dissociates producing radicals or other reactive species. The gas mixture will also generally contain gases suitable to provide hydrogen or a halogen in atomic form.

The dissociation of the source gas is preferably carried out using microwave energy in a reactor examples of which are known in the art. However, the transfer of any impurities from the reactor should be minimised. A microwave system may be used to ensure that the plasma is placed away from all surfaces except the substrate surface on which diamond growth is to occur and its mount. Examples of a preferred mount materials are: molybdenum, tungsten, silicon and silicon carbide. Examples of preferred reactor chamber materials are stainless steel, aluminium, copper, gold and platinum.

A high plasma power density should be used, resulting from high microwave power (typically 3-60kW, for substrate diameters of 25-300 mm) and high gas pressures ($50-500 \times 10^2 \text{Pa}$, and preferably $100-450 \times 10^2 \text{Pa}$).

Using the above conditions it has been possible to produce thick high quality single crystal CVD diamond gemstones with a desirable fancy colour using nitrogen additions to the gas flow in the range 0.1 to 500ppm.

An example of the invention will now be described:

EXAMPLE 1

Substrates suitable for synthesising single crystal CVD diamond of the invention may be prepared as follows:

- i) Selection of stock material (type Ia natural stones and type Ib HPHT stones) was optimised on the basis of microscopic investigation and birefringence imaging to identify substrates which were free of strain and imperfections.
- ii) Laser sawing, lapping and polishing to minimise subsurface defects using a method of a revealing plasma etch to determine the defect levels being introduced by the processing.
- iii) After optimisation it was possible routinely to produce substrates in which the density of defects measurable after a revealing etch is dependent primarily on the material quality and is below $5 \times 10^3/\text{mm}^2$, and generally below $10^2/\text{mm}^2$. Substrates prepared by this process are then used for the subsequent synthesis.

A high temperature/high pressure synthetic type 1b diamond was grown in a high pressure press, and as a substrate using the method described above to minimise substrate defects to form a polished plate 5 x 5mm square by 500µm thick, with all faces {100}. The surface roughness R_q at this stage was less than 1 nm. The substrate was mounted on a tungsten substrate using a high temperature diamond braze. This was introduced into a reactor and an etch and growth cycle commenced as described above, and more particularly:

- 1) The 2.45 GHz reactor was pre-fitted with point of use purifiers, reducing unintentional contaminant species in the incoming gas stream to below 80 ppb.
- 2) An *in situ* oxygen plasma etch was performed using 15/75/600 sccm (standard cubic centimetre per second) of $O_2/Ar/H_2$ at 263×10^2 Pa and a substrate temperature of 730°C.
- 3) This moved without interruption into a hydrogen etch with the removal of the O_2 from the gas flow.
- 4) This moved into the growth process by the addition of the carbon source (in this case CH_4) and dopant gases. In this instance was CH_4 flowing at 42 sccm and 3 ppm N in the gas phase.
- 5) On completion of the growth period, the substrate was removed from the reactor and the CVD diamond layer removed from the substrate.

- 6) This layer, identified as FN-1 was then polished to produce a 6 x 6 x 3 mm square cut synthetic diamond with weight 1.1 ct and certified by a professional diamond grader to have a desirable fancy light pink brown colour.
- 7) FN-1 was further characterised by the data provided below:
 - i) Optical absorption showing the characteristic broad peaks at 270 nm, 350 nm and 510 nm.
 - ii) Room temperature at 300K and 80K showing the N-V related centre.
 - iii) The EPR spectra showing single substitutional nitrogen with concentration 0.3 ppm and no $g=2.0028$ line.
 - iv) X-ray rocking curves map, showing the angular spread of the sample to be less than 20 arcsec.
 - v) Raman spectrum showing a line width (FWHM) to be about 2 cm^{-1} .
 - vi) SIMS showed a total nitrogen concentration of 0.35 ppm
 - vii) The CL spectra shows a substantial free exciton.

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OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C.
ATTORNEYS AT LAW
1940 DUKE STREET
ALEXANDRIA, VIRGINIA 22314 U.S.A.
(703) 413-3000